A ONE-POT FORMATION OF THE ANALOGUES OF CHERYLLINE- AND LATIFINE-TYPE 4-ARYL-1,2,3,4-TETRAHYDROISOQUINOLINES

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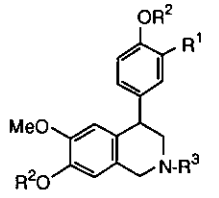
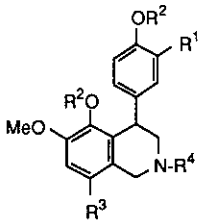
Abstract - The cyclization reaction of N-(2-bromo-4,5-dimethoxybenzyl)-1-(4-methoxyphenyl)-2-aminoethanol (9) with conc. H_2SO_4, 80% H_2SO_4, or conc. HCl-benzene yielded cherylline analogues (5) and/or (6) along with latifine analogues (7) and/or (8) according to the biogenetic route.

4-Aryl-1,2,3,4-tetrahydroisoquinolines have been long attractive because of their potential biological activities.[1] One of them, cherylline (1)[2,3] is a rare compound in Amaryllidaceae alkaloids and its synthesis has been performed by many organic chemists.[4] Recently, the biogenetic isomer of 1, latifine (2), was isolated and the racemic 2 was synthesized from a bromonorbelladine (3) via a latifine analogue (4) by us[6] and by Takano and co-workers.[7] We now describe the interesting one-pot formation of cherylline-type (C-type) analogues (5) and/or (6) along with latifine-type (L-type) analogues (7) and/or (8) by cyclization of a 1-phenyl-2-aminoethanol (9) with conc. H_2SO_4, 80% H_2SO_4, or conc. HCl-benzene under mild conditions according to the biogenetic route (Scheme 1).

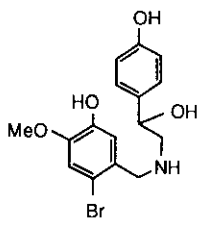
The 2-aminoethanol (9) prepared from a benzaldehyde (10) and O-methyloctopamine (11) was treated with conc. HCl-EtOH in the same way as for 3[6] to give an O-ethyl derivative (12) of 9 but no cyclization product. Thus, the compound (9) was treated with conc. H_2SO_4 at room temperature according to the method reported by Trepanier and Sunder.[1b] The resulting products were found to be the C-type compound (5) (45% yield) with a bromine atom at C-3' and (6) (5% yield) without a bromine atom, and the L-type compound (7) (9.9% yield) with dibromine atoms at C-3' and C-8. But no expected product (8) was obtained under these conditions. Similar treatment of 9



(1) R^1=R^2=H, R^3=Me
(14) R^1=H, R^2=R^3=Me
(16) R^1=Br, R^2=Me, R^3=CHO

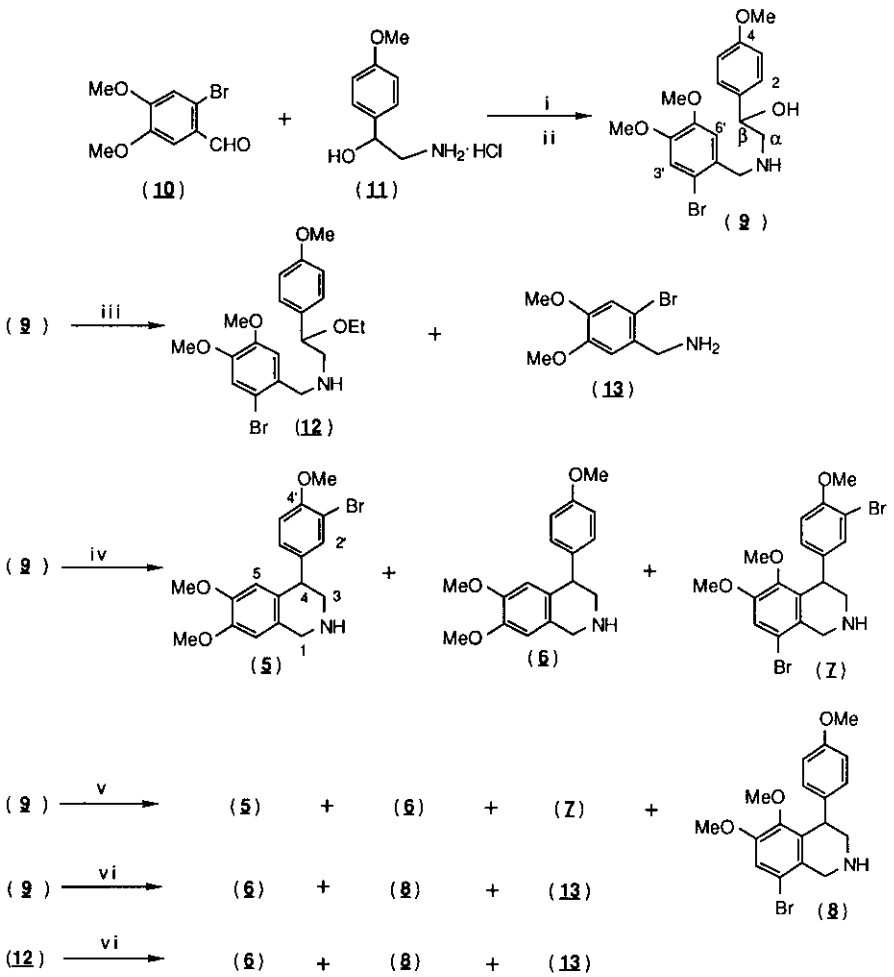


(2) R^1=R^2=R^3=H, R^4=Me
(4) R^1=R^2=R^4=H, R^3=Br
(15) R^1=R^3=H, R^2=R^4=Me
(17) R^1=R^3=Br, R^2=Me, R^4=CHO



(3)

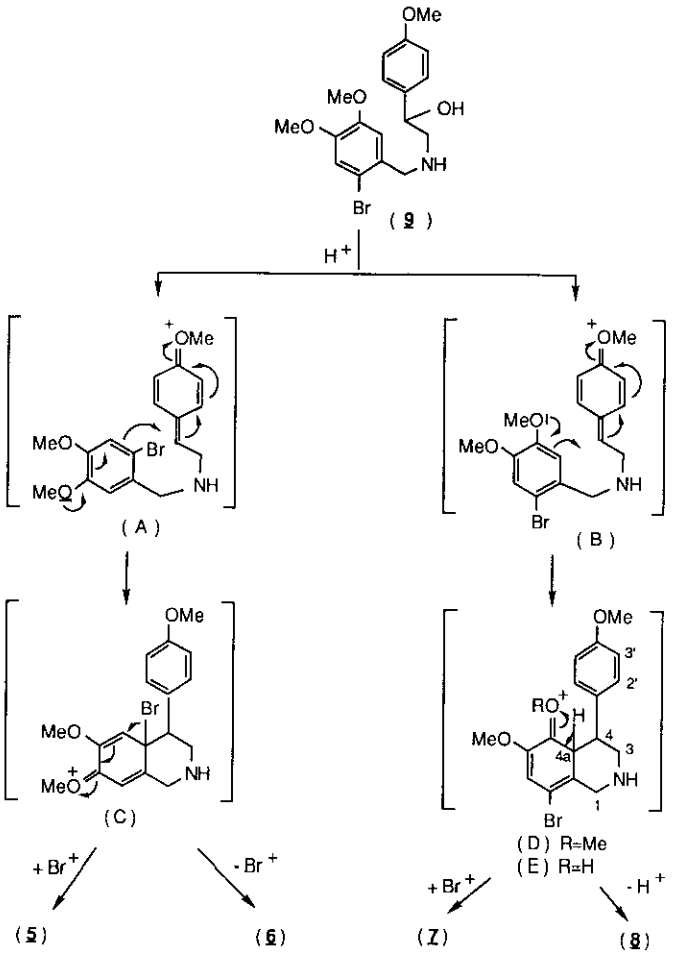
Chart 1



Scheme 1 Reagents: i, Δ; ii, $NaBH_4$; iii, conc. HCl-EtOH, reflux, 1.5 h; iv, conc. H_2SO_4, room temp., 1.5 h; v, 80% H_2SO_4, room temp., 1.5 h; vi, conc. HCl-benzene, 50 °C, 2 h

with 80% H_2SO_4 gave the C-type compounds (5) (19.2% yield) and (6) (9.6% yield), and the L-type compounds (7) (10.6% yield) and (8) (14% yield) with a bromine atom at C-8. Furthermore, the reaction of 9 with conc. HCl-benzene[4f] at 50°C gave the C-type compound (6) (22.9% yield) and the L-type compound (8) (21.5% yield) along with a benzylamine (13) (19.8% yield). Similarly, the O-ethyl-2-aminoethanol (12) was treated with conc. HCl-benzene to give 6, 8 and 13 in yields of 17.3, 9.2 and 19.3%, respectively. The structures of these products (5), (6), (7) and (8) were determined by their mass and ^{1}H-nmr spectra (see Experimental). Especially, the chemical shifts (δ3.35 and 3.28) of the methoxy groups at C-5 in 7 and 8 showed the compounds to have L-type structures.[4,5] The bromine atom of the 4-phenyl group in 5 and 7 was concluded to be located at C-3' for the following reasons. i) The nuclear Overhauser effect (NOE) increments (20.5 and 21.0%) between the protons (δ3.85 and 3.84) of the methoxy group and the doublet (J=8Hz) (but not a double of doublet) of H-5' (δ6.79 and 6.77, respectively) were observed. ii) This was also supported by the consideration of the directive effect of the methoxy group and of the steric hindrance (especially in 7) of a bromine atom at C-2'. In addition, the structures of the novel products (5) and (7) were confirmed by their conversions to racemic O,O-dimethylcherylline (14)[3] and O,O-dimethyllatifine (15)[6] via the corresponding N-formyl derivatives (16) and (17).

These results suggest the mechanism for these cyclization reactions as shown in Scheme 2. Dehydration of 9 with an acid gives quinonoide intermediates[4c] (A) and (B). Then, the L-type compounds (7) and (8) may be formed via a intermediate (D), which has more steric hindrance than a intermediate (E) (which may be formed in the synthesis of racemic 4[6] from the 2-aminoethanol (3)), because of the peri-like position between the 5-methoxy group and the 4-phenyl group. Elimination of the proton at C-4a in D gives the monobromo-compound (8) and an intermolecular electrophilic attack of a bromonium ion (generated from a intermediate (C) as described below) on C-3' in 8 affords the dibromo-compound (7). On the other hand, the C-type products (5) and (6) may be formed via the intermediate (C), which has some steric hindrance due to the two bulky groups at ortho positions (C-4a and C-4) and which has more poor leaving group, a bromonium ion, at C-4a than a proton in E. In the cyclization reaction of 9 with conc. H_2SO_4, the intermediate (C) seems to be formed mainly, while with 80% H_2SO_4 or conc. HCl-benzene both the intermediates (C) and



Scheme 2

(D) seem to be formed equally on the basis of their cyclization products. A bromine atom has been used as a protecting group in cyclization reactions,[6,8] but we found that under the conditions as described above the bromine atom of 9 left via the intermediate (C) and was not available as a protecting group.

EXPERIMENTAL

All melting points are given as uncorrected values. Infrared (ir) spectra were taken with a Hitachi IR-215 spectrophotometer and are given in cm^{-1}. High-resolution mass (ms) spectra were recorded on a JEOL JMS-D 300 spectrophotometer. Proton nuclear magnetic resonance (^{1}H-nmr) spectra were recorded on a JEOL-PS-100 spectrometer in $CDCl_3$ with tetramethylsilane as a standard and are given in δ values. The plates used for preparative tlc (PLC) were coated with silica gel (PF_{254} Merck).

N-(2-Bromo-4,5-dimethoxybenzyl)-1-(4-methoxyphenyl)-2-aminoethanol (9)

A mixture of 6-bromoveratraldehyde (10) (500 mg, 2.04 mmol), O-methyloctopamine hydrochloride (11)[9] (415 mg, 2.04 mmol), K_2CO_3 (1.123 g, 8.14 mmol), and EtOH (50 ml) was refluxed for 2.5 h. Sodium borohydride ($NaBH_4$) (660 mg, 17.5 mmol) was added under ice-cooling and then the mixture was refluxed for 2 h. The solvent was evaporated *in vacuo*. H_2O (40 ml) was added and the mixture was extracted with $CHCl_3$. The extract was washed with H_2O, dried ($MgSO_4$), and evaporated to give a white powder (807 mg). Recrystallization from EtOH-ethyl acetate-diethyl ether gave 9 (534 mg, 72.1%) as colourless needles, mp 119-121°C. Ir(KBr): 3300 and 3130. ^{1}H-Nmr: 7.24 and 6.82 (each 2H,d,J=8Hz,H-2 and H-6, and H-3 and H-5), 6.96 and 6.87 (each 1H,s,H-3' and H-6'), 4.70 (1H,dd,J=8 and 4Hz,H-β), 3.83 (6H,s,OCH_3-4' and OCH_3-5'), 3.78 (2H,br s,ArCH_2N), 3.76 (3H,s,OCH_3-4), 3.46 (2H,br s,NH and OH), 2.78 (2H,m,CH_2-α). Anal. Calcd for $C_{18}H_{22}BrNO_4 \cdot 1/2H_2O$: C,53.34;H,5.72;N,3.46. Found: C, 53.08;H,5.62;N,3.72.

Reaction of 9 with conc. Hydrochloric Acid in EtOH

A solution of 9 (438 mg, 1.11 mmol) in conc. HCl (12 ml, 0.12 mol) and EtOH (36 ml) was refluxed for 1.5 h. The solvent was evaporated *in vacuo* and H_2O (72 ml) was added. The mixture was washed with diethyl ether, made basic with NH_4OH, and extracted with $CHCl_3$. The extract was washed with H_2O, dried ($MgSO_4$), and evaporated to give an oil (345 mg). This crude product was subjected to PLC in $CHCl_3$-MeOH (20:1). The fraction of Rf 0.20-0.23 gave 13 (32.2 mg, 11.9%) as an oil. ^{1}H-Nmr: 6.98 and 6.91 (each 1H,s, H-3 and H-6), 3.86 (8H,s,2xOCH_3 and ArCH_2N), 2.50 (2H,br s,NH_2). Ms(m/z): Calcd for $C_9H_{12}BrNO_2$: 245.0052 (M^+), 247.0032 (M+2). Found: 245.0072 (M^+), 247.0069 (M+2). The fraction of Rf 0.26-0.32 gave 12 (257 mg, 54.8%) as an oil. ^{1}H-Nmr: 7.21 and 6.85 (each 2H,d,J=9Hz,H-2 and H-6, and H-3 and H-5), 6.94 and 6.97 (each 1H,s,H-3' and H-6'), 4.39 (1H,dd,J=8 and 4Hz,H-β), 3.84 (6H,s,OCH_3-4' and OCH_3-5'), 3.81 (2H, br s,ArCH_2N), 3.78 (3H,s,OCH_3-4), 3.75 (2H,q,J=7Hz,OCH_2CH_3), 2.90 (1H,dd,J=12 and 8Hz,

H-α), 2.37 (1H,s,NH), 1.16 (3H,t,J=7Hz,$OCH_2\underline{CH_3}$). Ms(m/z) (M+1): Calcd for $C_{20}H_{26}BrNO_4$: 424.1123. Found: 424.1098.

Reaction of 9 with conc. Sulfuric Acid

The ethanolamine 9 (164.8 mg, 0.42 mmol) was dissolved in H_2SO_4 (10 ml, 0.10 mol) under ice-cooling and the solution was stirred at room temperature for 1.5 h. The reaction mixture was poured into ice water (20 ml) and made basic with solid NaOH. The mixture was extracted with $CHCl_3$. The extract was washed with H_2O, dried ($MgSO_4$), and evaporated to give an oil, which was subjected to PLC in $CHCl_3$-EtOH (15:1). The fraction of Rf 0.32-0.44 gave the isoquinoline (5) (70.7 mg, 45.0%) as an oil. ^{1}H-Nmr: 7.27 (1H, d,J=2Hz,H-2'), 6.97 (1H,dd,J=8 and 2Hz,H-6'), 6.79 (1H,d,J=8Hz,H-5'), 6.55 (1H,s, H-8), 6.33 (1H,s,H-5), 4.02 (3H,m,H-1 and H-4), 3.85 (6H,s,OCH_3-7 and OCH_3-4'), 3.68 (3H,s,OCH_3-6), 3.55 (1H,dd,J=13 and 5Hz,H-3), 2.98 (1H,dd,J=13 and 7Hz,H-3), 3.12 (1H,s,NH). Ms(m/z): Calcd for $C_{18}H_{20}BrNO_3$: 377.0634 (M^+), 379.0605(M+2). Found: 377.0593 (M^+), 379.0567 (M+2). The fraction of Rf 0.63-0.67 gave the isoquinoline (7) (18.9 mg, 9.9%) as an oil. ^{1}H-Nmr: 7.24 (1H,d,J=2Hz,H-2'), 7.06 (1H,s,H-7), 6.92 (1H,dd,J=8 and 2Hz,H-6'), 6.77 (1H,d,J=8Hz,H-5'), 4.17 (1H,m,H-4), 3.91 and 3.80 (each 1H,d,J=17Hz,CH_2-1), 3.84 (3H,s,OCH_3-4'), 3.82 (3H,s,OCH_3-6), 3.35 (3H,s,OCH_3-5), 3.11 (2H,m,CH_2-3), 1.90 (1H,s,NH). Ms(m/z): Calcd for $C_{18}H_{19}Br_2NO_3$: 453.9655 (M-1), 456.9713 (M+2), 458.9690 (M+4). Found:453.9680 (M-1), 456.9756 (M+2), 458.9668 (M+4). The fraction of Rf 0.54-0.60 gave the isoquinoline (6)(6.1 mg, 5.0%) as an oil. This compound (6) was identical with 6 obtained by the treatment of 9 with 80% H_2SO_4 as described below by comparison of their ^{1}H-nmr spectra.

Reaction of 9 with 80% Sulfuric Acid

The ethanolamine 9 (150 mg, 0.38 mmol) was dissolved in 80% H_2SO_4 (10 ml, 81 mmol) under ice-cooling and stirred at room temperature for 1.5 h. Work-up in the usual way gave a crude product (159.2 mg). This was subjected to PLC in $CHCl_3$-MeOH (15:1) to give four fractions. The fractions of Rf 0.33-0.43 and Rf 0.69-0.73 gave 5 (29.2 mg, 19.2%) and 7 (18.3 mg, 10.6%), respectively. The fraction of Rf 0.20-0.31 gave 6 (26 mg, 22.9%) as an oil. ^{1}H-Nmr: 7.00 (2H,d,J=8Hz,H-2' and H-6'), 6.80 (2H,d,J=8Hz, H-3' and H-5'), 6.54 (1H,s,H-8), 6.35 (1H,s,H-5), 4.05 (3H,m,CH_2-1 and H-4), 3.84 (3H, s,OCH_3-7), 3.77 (3H,s,OCH_3-4'), 3.65 (3H,s,OCH_3-6), 3.36 and 3.02 (each 1H,dd,J=12 and 6Hz,CH_2-3), 2.16 (1H,s,NH). Ms(m/z)(M^+): Calcd for $C_{18}H_{20}NO_3$: 299.1522. Found: 299.1563. The fraction of Rf 0.66-0.69 gave 8 (30.9 mg, 21.5%) as an oil. ^{1}H-Nmr: 7.03 (1H,s,H-7), 6.94 (2H,d,J=8Hz,H-2' and H-6'), 6.76 (2H,d,J=8Hz,H-3' and H-5'),

4.19 (1H,m,H-4), 3.89 and 3.78 (each 1H,d,J=17Hz,CH_2-1), 3.78 (3H,s,OCH_3-6), 3.74 (3H,s,OCH_3-4'), 3.28 (3H,s,OCH_3-5), 3.08 (2H,m,CH_2-3), 1.94 (1H,s,NH). Ms(m/z): Calcd for $C_{18}H_{19}BrNO_3$: 376.0546 (M-1), 378.0529 (M+1). Found: 376.0499 (M-1), 378.0550 (M+1). The products (5) and (7) were identical with authentic samples of 5 and 7 obtained as above by comparisons of their ^{1}H-nmr spectra.

Reaction of 9 with conc. Hydrochloric Acid in Benzene

A mixture of 9 (150.7 mg, 0.38 mmol), conc. HCl (15 ml, 0.15 mol) and benzene (30 ml) was stirred at 50°C for 2 h. The aqueous layer was washed with benzene and made basic with solid Na_2CO_3. The mixture was extracted with $CHCl_3$. The extract was washed with H_2O, dried ($MgSO_4$) and evaporated to give an oil (120.3 mg). This crude product was subjected to PLC in $CHCl_3$-MeOH (10:1) to give three fractions. Each fraction of Rf 0.33-0.44, Rf 0.47-0.57, and Rf 0.63-0.73 gave 13 (22 mg, 19.8%), 6 (26 mg, 22.9%) and 8 (30.9%) as oily products, respectively. These products (13), (6) and (8) were identical with those obtained as above by comparisons of their ^{1}H-nmr spectra.

Reaction of 12 with conc. Hydrochloric Acid in Benzene

A mixture of 12 (139.2 mg, 0.33 mmol), conc. HCl (15 ml, 0.15 mol) and benzene (30 ml) was stirred at 50°C for 2 h. Work-up in the same way as 9 gave a crude oil (74.7 mg), which was subjected to PLC in $CHCl_3$-MeOH (10:1). The fractions of Rf 0.35-0.47, Rf 0.50-0.54 and Rf 0.60-0.67 gave 13 (18.8 mg, 19.3%), 6 (16.9 mg, 17.3%) and 8 (11.4 mg, 9.2%) as oily products, respectively. These products (13), (6) and (8) were identical with those obtained from 9 as above by comparisons of their ^{1}H-nmr spectra.

6,7-Dimethoxy-N-formyl-4-(3'-bromo-4'-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (16)

A mixture of 5 (20.8 mg, 0.055 mmol), $MgSO_4$ (142 mg, 1.18 mmol), K_2CO_3 (141 mg, 1.02 mmol) and ethyl formate-EtOH (3:1) (7 ml) was refluxed for 3 h. The mixture was filtered and the filtrate was concentrated. 2% HCl (7 ml) was added and the mixture was extracted with $CHCl_3$. The extract was washed with H_2O, dried ($MgSO_4$), and evaporated to give 16 (15.9 mg, 71.2%) as an oil. ^{1}H-Nmr: 8.21 and 7.76 (1H, each s,CHO), 7.28 (1H,s,H-2'), 6.78 (2H,s,H-5' and H-6'), 6.64 (1H,s,H-8), 6.38 (1H,s,H-5), 4.96 and 4.40 (each 1H,d,J=17Hz,CH_2-1), 4.04 (1H,m,H-4), 3.80-3.40 (2H,m,CH_2-3), 3.87 (3H,s,OCH_3-4'), 3.84 (3H,s,OCH_3-7), 3.72 (3H,s,OCH_3-6). Ms(m/z)(M+2): 407.0556. Found: 407.0536.

8-Bromo-N-formyl-5,6-dimethoxy-4-(3'-bromo-4'-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (17)

A mixture of 7 (27.6 mg, 0.06 mmol), $MgSO_4$ (200 mg, 1.66 mmol), K_2CO_3 (200 mg, 1.45 mmol) and ethyl formate-EtOH (3:1) (10 ml) was refluxed for 5 h. Work-up in the same way as 5 gave 17 (25.9 mg, 88.4%) as an oil. ^{1}H-Nmr: 8.24 and 7.62 (1H,each s,CHO), 7.32 (1H,d,J=2Hz,H-2'), 7.12 (1H,s,H-7), 6.70 (2H,s,H-5' and H-6'), 5.27 and 4.32 (each 1H,d,J=18Hz,CH_2-1), 4.08 (1H,m,H-4), 3.58 (2H,m,CH_2-3), 3.82 (6H, s,OCH_3-6 and OCH_3-4'), 3.36 (3H,s,OCH_3-5). Ms(m/z): Calcd for $C_{19}H_{19}Br_2NO_4$: 482.9679 (M^+), 484.9660 (M+2), 486.9649 (M+4). Found: 482.9646 (M^+), 484.9642 (M+2), 486.9662 (M+4).

Synthesis of Racemic O,O-Dimethylcherylline (14) from 16

To a solution of 16 (17.8 mg, 0.044 mmol) in dry THF (10 ml) was added $LiAlH_4$ (152 mg, 4.0 mmol) and the mixture was refluxed for 1.5 h under stirring. A saturated solution of sodium potassium tartrate in H_2O was added. The mixture was extracted with $CHCl_3$. The extract was washed with H_2O, dried ($MgSO_4$), and evaporated to give an oil (17.5 mg). The crude product was subjected to PLC in $CHCl_3$-MeOH (15:1). The fraction of Rf 0.39-0.47 gave 14 (12.3 mg, 89.8%) as an oil (lit. mp 82-83°C,[3] mp 87-89°C[2b]). ^{1}H-Nmr: 7.08 (2H,d,J=8Hz,H-2' and H-6'), 6.80 (2H,d,J=8Hz,H-3' and H-5'), 6.54 (1H,s,H-8), 6.34 (1H,s,H-5), 4.13 (1H,dd,J=8 and 6Hz,H-4), 3.84 (3H,s, OCH_3-4'), 3.78 (3H,s,OCH_3-7), 3.63 (3H,s,OCH_3-6), 3.58 (2H,br s,CH_2-1), 2.97 (1H, dd,J=12 and 6Hz,H-3), 2.47 (1H,dd,J=12 and 8Hz,H-3), 2.40 (3H,s,NCH_3). Ms(m/z)(M^+): Calcd for $C_{19}H_{23}NO_3$: 313.1675. Found: 313.1635. This compound (14) was identical with an authentic 14[3] by comparison of their ^{1}H-nmr spectra.

Synthesis of Racemic O,O-Dimethyllatifine (15) from 17

To a solution of 17 (32.7 mg, 0.068 mmol) in dry THF (25 ml) was added $LiAlH_4$ (1.0 g, 26 mmol) and the mixture was refluxed for 2 h under stirring. Work-up in the same way as 16 gave 15 (6.0 mg, 28.4%) as colourless crystals, mp 85-89°C (lit.[6] oil). ^{1}H-Nmr: 7.10 (2H,d,J=8Hz, H-2' and H-6'), 6.80 (2H,s,H-7 and H-8), 6.75 (2H,d,J=8Hz,H-3' and H-5'), 4.26 (1H,m,H-4), 3.80 (2H,br s,CH_2-1), 3.77 (3H,s, OCH_3-6), 3.73 (3H,s,OCH_3-4'), 3.18 (3H,s,OCH_3-5), 2.70 (2H,m,CH_2-3), 2.32 (3H,s, NCH_3). Ms(m/z)(M^+): 313.1675. Found: 313.1664. This compound (15) was identical with an authentic 15[6] by comparison of their ^{1}H-nmr spectra.

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